Refrigerant Concentrations in Car Passenger Compartments*

Ian Maclaine-cross
The University of New South Wales, Sydney, Australia

Abstract

Maximum refrigerant concentrations can be predicted from measured charge, leaks, volume and ventilation by simple formulae. Refrigerant 290/600a is a popular 'drop-in' replacement for 12, 134a and 406a in car air conditioners. Physically possible but improbable leaks of R290/600a into the passenger compartment give concentrations above the lower explosive limit for four out of ten Australian cars tested. Simple precautions like placing the expansion valve in the engine bay avoid this.

1 Introduction

A common driver error is failure to see through a misted windscreen. The Australian demister performance standard (FORS 1995) effectively requires fresh air flow into the passenger compartment about 100 L/s. The fresh air required for five occupants with smoking is over 100 L/s. Some manufacturers have increased fresh air well above the minimum for demister performance. Moving the expansion valve into the engine bay (Figure 1) makes a distracting cloud of refrigerant from any passenger compartment failure impossible. These design changes and many others incidentally reduce possible maximum refrigerant concentrations in the passenger compartments of late model cars.

R12 previously used for car air conditioners has a practical limit (BS4434–1995) of 500 g/m^3. The practical limits for the replacements refrigerants 134a, 406a, 290/600a and 600a are 250, 100, 8 and 8 g/m^3, respectively. R290/600a refers here to commercial hydrocarbon mixtures with properties close to those of a 50/50 by mass mixture of propane (R290) and isobutane (R600a). R290/600a is flammable at room temperature and pressure above its lower explosive limit (LEL), 2% by volume, and below its upper explosive limit (UEL), 10%. An Australian code for R290/600a (IAHRA 1996) requires that any physically possible leak not exceed the LEL in the passenger compartment. R600a can reduce the energy consumption and halve the mass of a car air conditioner (Maclaine-cross and Leonardi 1997) but requires equipment redesign.

The maximum concentrations resulting from a typical leak can be calculated for any space and any refrigerant using the formulae in Section 2. The refrigerant charge (Section 3), leakage rate (Section 4) and mixing (Section 5) required are given for car

*Proceedings of the *International Conference on Ozone Protection Technologies*, Baltimore MD, pp. 403–412, November 12–13, 1997.

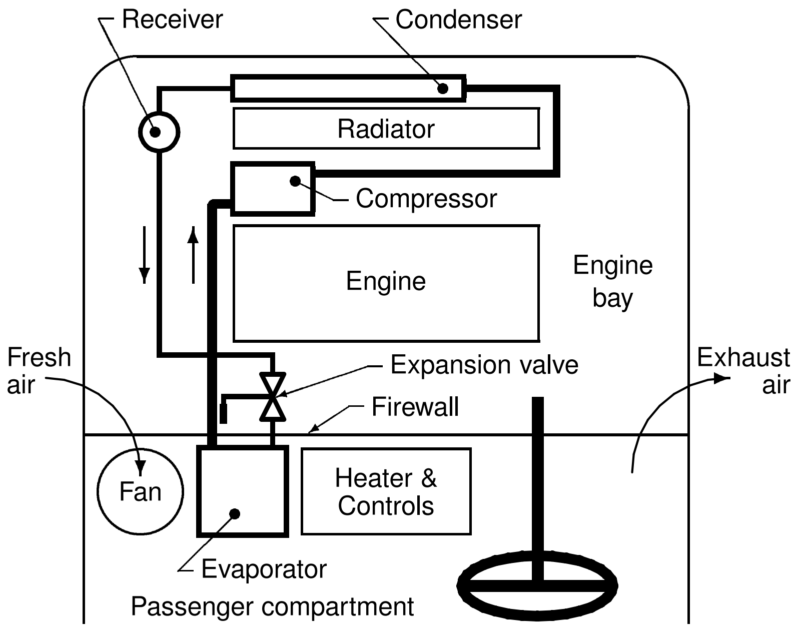

Figure 1: Schematic of car air conditioner with liquid line receiver and expansion valve in engine bay (right hand drive).

passenger compartments and air conditioners using R290/600a unless specified otherwise. With volume and fresh air flows (Section 6) the peak mean concentrations then calculated (Section 7) suggest recommendations for using R290/600a (Section 8).

2 Calculation of Maximum Concentrations

Figure 2 shows refrigerant leaking into an enclosed ventilated space. Pressure and temperature changes are assumed small compared with absolute except within millimetres of a leak. The volume concentration in exhaust air is assumed close to the mean volume concentration, c.

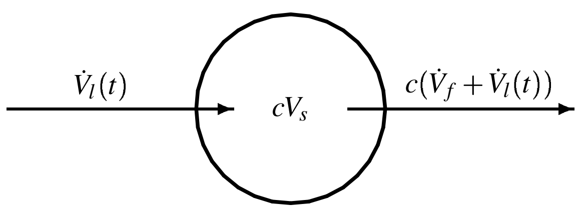

Figure 2: Schematic of refrigerant flows in and out of an enclosed ventilated space.

Conservation of refrigerant mass in the space gives the following ordinary differential equation for the mean volume concentration of refrigerant, c, in the compartment as a function of time, t:

$$V_s \frac{\mathrm{d}c}{\mathrm{d}t} = (1-c)\dot{V}_l(t) - c\dot{V}_f \tag{1}$$

where $\dot{V}_f$ is the volume flow rate of fresh air and V_s is the volume of the space. The volume flow rate of refrigerant into the space, $\dot{V}_l(t)$, is a known function of time depending on initial leakage rate, $\dot{V}_{li}$, and the total volume of the charge, V_c, at the temperature and pressure of the space. The boundary condition used here in solving Equation 1 is $c = 0$ when $t = 0$.

The maximum average concentration of refrigerant in the space, $c_{\max}$, and the time at which it occurs, $t_{\max}$ are functions of V_c/V_s and $\dot{V}_{li}/\dot{V}_f$ which can be determined by solving Equation 1.

2.1 Constant leak rate

For a leak rate $V_l(t)$ which is constant from $t = 0$ until $t = V_c/\dot{V}_{li}$ at $V_l(t) = V_{li}$, Equation 1 has the exact solutions:

$$t_{\max} = V_c/\dot{V}_{li}$$

$$c_{\max} = \left(1 - \exp\left(-\left(1 + \frac{\dot{V}_f}{\dot{V}_{li}}\right)\frac{V_c}{V_s}\right)\right) / \left(1 + \frac{\dot{V}_f}{\dot{V}_{li}}\right) \tag{2}$$

Slow refrigerant leaks occurring over hours are usually at a constant rate.

2.2 Declining ramp leak rate

A leak rate zero except between $t = 0$ and $t = 2V_c/\dot{V}_{li}$ where $V_l(t) = \dot{V}_{li}(1 - t\dot{V}_{li}/(2V_c))$ is a declining ramp. For $c_{\max} \leq 0.1$, the following formula for $c_{\max}$ is within 1% of exact numerical solutions:

$$t_{\max} = \frac{V_s}{\dot{V}_f}\ln\left(1 + \frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right)$$

$$c_{\max} = 1/\left(1 + \frac{\dot{V}_f}{\dot{V}_{li}}/\left(1 - \ln\left(1 + \frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right)/\frac{2V_c\dot{V}_f}{V_s\dot{V}_{li}}\right)\right) \tag{3}$$

Rapid refrigerant leaks occurring over minutes are usually close to a declining ramp. BS 4434–1995, Clause 1.3.70, defines a *sudden major release* as the majority of the refrigerant charge being released in under five minutes. The initial leakage rate for this to occur, $\dot{V}_{li} = V_c(2 - \sqrt{2})/300$. Figure 3 shows an example of a sudden major release and the resulting concentrations.

3 Refrigerant Charge

The charge is the mass of refrigerant circulating in a system. There is always a minimum charge for satisfactory operation. The system should operate equally well with the initial charge added when the refrigerant is replaced. The minimum charge can be less than 25% of the initial charge in a car air conditioner. The difference between the initial and minimum charges is an allowance for leakage. Often the initial charge of a replacement refrigerant has about the same liquid volume as the R12 it replaces.

When an equal liquid volume of the hydrocarbon mixture R290/600a replaces R12 in a car air conditioner the suction superheat is often 1 K or less. The suction superheat

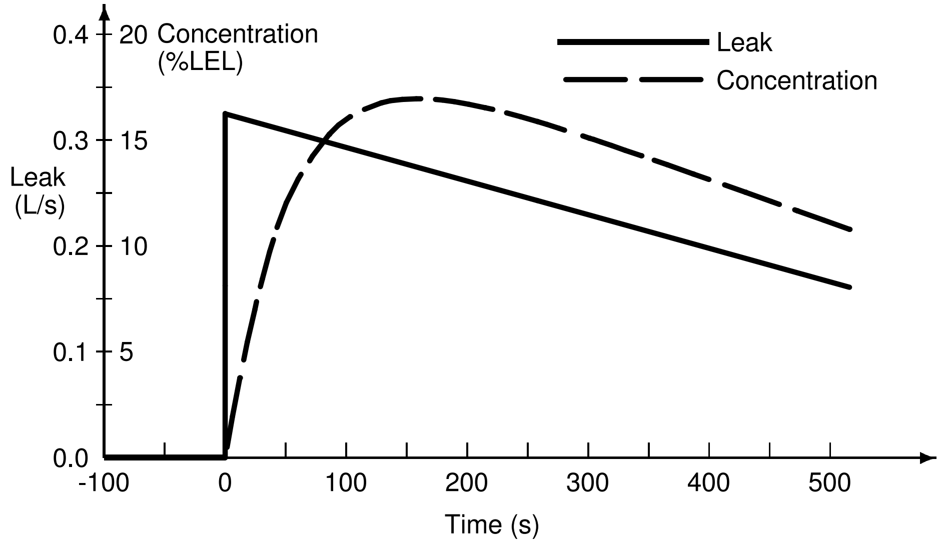

Figure 3: R290/600a flow rate and concentration as a function of time for a sudden major release into the passenger compartment of a 1984 Pulsar with fan on and fresh air vent open (Tables 2 and 4).

is increased if a lower initial charge is used. A third the mass of the R12 initial charge is used. The large size of R290 and R600a molecules reduces diffusion through elastomers so recharge intervals are similar to R12.

R600a vapour has over four times the specific volume of R12 allowing the minimum charge mass to be more than halved. Its leakage speed is less than half R12 and its molar volume is 13% larger (Maclaine-cross and Leonardi 1997) halving the required leakage allowance also. The initial charge mass of an R600a car air conditioner should be less than a fifth of an R12 car conditioner of similar cooling capacity.

4 Leaks and Leakage

Table 1 shows leakages through orifices from a car air conditioner of about 3.5 kW cooling capacity operated on a test bed (Cai 1996). The orifices were on either the liquid line just upstream of the expansion valve or the suction line just downstream of the evaporator and were controlled by a 90° ball valve. After the orifice, a 15 mm inside diameter coil submerged in water at room temperature reheated the R290/600a before weighing in an aluminized polymer bag mounted on electronic scales. The charging cylinder was weighed before and after charging and the differences were close to the mass of refrigerant in the bag at the end of the test confirming measuring accuracy.

The time for 50% of the liquid to escape through the 2 mm orifice was longer than through a 1 mm orifice (Table 1). The refrigerant flashed from the liquid line receiver reducing the density of the fluid flowing through the orifice. Liquid flow rates calculated using line pressure and assuming liquid entering the orifice confirmed this. The poor agreement between predicted and measured maximum vapour flow rates is believed due to errors in orifice dimensions and liquid slugging.

Table 1: Measured and predicted leakage of R290/600a through circular orifices from a 3.5 kW car air conditioner operating on a test bed (Cai 1996).

Line with orifice	Liquid		Vapour		
Orifice diameter (mm)	1	2	1	2	3
Refrigerant charged (g)	356	229	271	325	262
Refrigerant collected (g)	321	225	271	330	251
50% collection time (s)	10	11	180	50	25
90% collection time (s)	50	27	370	110	70
Finish of collection (s)	74	34	480	236	100
Peak measured flow (g/s)	15.1	12.3	0.98	6.8	5.1
Predicted peak flow (g/s)	24.6	96.1	0.66	2.7	6.4

The physically possible failures resulting in loss of refrigerant to the passenger compartment depend on the design of the refrigerant containing components in the compartment:—

1. The structural layer of flexible hoses fatigues with formation of a blister in the sealing layer which then bursts.

2. An O-ring joint is overtightened, stripping the threads without causing an immediate leak.

3. Salt particles cause pinhole corrosion of the evaporator.

The above failures are each known to have occurred at least once in Australia in the last ten years. No examples of the following failures are known but they are believed possible from engineering science:—

4. A fatigue fracture progresses to a crack through the metal.

5. A mercury drop is allowed to rest in the evaporator forming a substantial volume of amalgam with the aluminium which later fractures under normal operating pressures.

For failure of hoses or O-rings in the passenger compartment, I assume frictional, isenthalpic, flashing flow from the receiver to the passenger compartment (Boucher and Alves 1973, Huber *et al.* 1996). For a liquid line with 8 mm internal diameter and a total pressure loss coefficient of 4 the initial flow rate calculated is 250 g/s with compressor on. The experiments of Cai (1996) (Table 1) and Tosovic (1996) suggest the actual flows might be lower. These failures occur when the pressure rises above a critical value so they may occur immediately after the air conditioner is turned off but they do not occur while the engine is off and cooling.

When a corrosion pinhole in an evaporator reaches 0.1 mm the leakage rate is about 10 mg/s when the air conditioner is operating which causes the largest charge (Table 4, 433 g) to leak out in about 12 hours. If the air conditioner is off the leakage rate is about 20 g/s because the pressure in the evaporator doubles. The pinhole has no chance to grow larger since the failed evaporator would certainly be replaced with such a leak rate.

Fatigue fractures grow infinitesimally each stress cycle. Passenger compartment components are subjected to about ten stress cycles an hour. If a vehicle has an operating life of 20,000 hours this is 200,000 cycles of stress. The liquid line is of greatest concern because the same size crack leaks liquid at about 15 times the mass flow rate for vapour. The BS 4434–1995 allowable pressure is 1.7 MPa causing a 9 MPa hoop stress in a 10 mm liquid line. The 500 million cycle fatigue strength for the softest temper of 5152 aluminium tubing alloy is 90 MPa (ADC 1973). The factor of safety for simple fatigue is more than 10 so no such failures are possible in even soft metal.

With a high stress concentration such as at a scratch, other damage or poor design feature, crack growth and then refrigerant leakage may occur at much lower stresses. Any crack will initially be so small that the leakage could not be detected but eventually the crack grows to 2 mm long. Fracture mechanics (Broek 1982, p. 12–13) predicts that a tensile stress about 400 MPa is required to make such a crack grow catastrophically. The stress at the 1.7 MPa allowable pressure is only 9 MPa so there is a factor of safety over 40 against this possibility.

A 9 MPa uniform stress will open the crack to 0.5 μm width (Broek 1982, eq. 3.59) and at the 1.7 MPa allowable pressure this will leak about 20 mg/s of liquid. When the air conditioner turns off both the gap and pressure are reduced and liquid evaporates leaving only vapour available to leak. Most leaking is with the air conditioner off and at about 1 mg/s of vapour which causes the largest charge to leak out in five days.

5 Mixing

All the refrigerant leaks described in Section 4 are jets submerged initially in air and then later in air/refrigerant mixture. They start at an orifice in the refrigerant circuit which is over 300 mm above the floor at the very front of the passenger compartment. If the fan is on, a leakage into the air duct will all enter the passenger compartment but a leakage outside the air duct may partly or completely leave by the exhaust vent in front of the driver. If the fan is off, all or part of the leakage may leave by the inlet vent as well as the exhaust vent. I assume all leakage mixes into the compartment.

All leaks start with 100% refrigerant concentration which is diluted towards the average concentration in the compartment. The momentum of the jet and natural thermal and density driven convection are always available to drive this mixing. If the compartment is occupied, natural and forced convection from the occupants and usually the fan and motion of the vehicle are also available. For a given orifice, a vapour jet will have a lower mass flow rate and a larger velocity.

Vapour leaks start at close to the velocity of sound in the refrigerant (about 200 m/s for R290/600a). Many measurements have been made of both the velocity and concentration distributions of such jets and the results correlated. Schlichting (1968) summarizes early work and Elias (1996) has applied these and later work to predicting the velocities and concentrations of jets from hydrocarbon refrigerant leaks.

Elias (1996) found a circular R290/600a leak into refrigerant free air had at the 2% LEL contour a velocity everywhere over 1 m/s. On the centreline the velocity was 5.4 m/s at the LEL which was only 200 mm from a 1 mm diameter orifice discharging 1.1

g/s. The flame velocity at the 2% LEL is 0.25 m/s so any flame requires a continuous source of ignition.

Liquid jets are possible only for systems with a liquid line entering the passenger compartment when the system is operating or has very recently operated. The maximum liquid velocity will be about 30 m/s for R290/600a. The liquid flashes to a vapour-liquid mixture at about -30°C . When the mixture has been diluted to the 10% UEL the liquid drops will have evaporated and the density difference is mainly thermal. The mixture falls to the front floor with further mixing and then flows to the rear of the passenger compartment where warming causes it to rise giving a general circulation.

For Razmovski (1994)'s liquid carbon dioxide releases described in Section 6 the sampling point was about the level of the exhaust vent on most of the vehicles. Ten experiments were performed on five Australian cars, half with fan off and vents closed. For all experiments, 80% of the peak concentration was reached within 18 s of opening the valve. On most the peak concentration was reached within 9 s of opening the valve.

The mixing assumption of Section 2 is well satisfied for refrigerant leaks into the passenger compartment.

6 Volume and Fresh Air

Razmovski (1994) and Rajasekariah (1995) measured the volume of and fresh air flows into the passenger compartments of ten Australian cars using carbon dioxide as a tracer. Carbon dioxide was selected as a tracer because its molecular mass is close to propane and instrumentation to measure its concentration was available.

The procedure was to purge, fill and weigh a 2 L fire extinguisher with typically 300 g of liquid carbon dioxide. The extinguisher was fitted with a 90° ball valve with 300 mm handle extension. The car was parked in a sheltered, shaded, outdoor position. The extinguisher was held orifice down by a laboratory stand on the floor in front of the passenger seat and opened by a string passing under the passenger door. The extinguisher orifice was 300 mm above the floor and discharged fully in less than 3 s. The air in the passenger compartment was sampled about 600 mm above the floor, level with the back of the front seats and on the centreline of the vehicle at 0.5 L/minute. The carbon dioxide concentration was measured by a Beckman 865 infrared analyzer outside the passenger compartment. The readings of the analyzer were recorded on a personal computer through a YEW datalogger every 9 s. The maximum wind velocity was always less than 3 m/s.

Table 2 gives the passenger compartment volume and fresh air flows calculated for various configurations of the ten Australian cars tested. The Kingswood and the Volvo air-conditioners did not have a fresh air vent and the Berlina had a fixed fresh air vent.

Razmovski (1994) also used this apparatus with a door switch and electronic timer to measure the loss in concentration when the driver's door was opened fully and closed again quickly without entering the vehicle. Table 3 shows this concentration loss is significant for many vehicles.

Table 2: Measured passenger compartment volume and total fresh air flows for ten Australian passenger cars (Razmovski 1994, Rajasekariah 1995). The first three configurations have all windows closed and the last three have the fan operating at full flow. The third (F.V.) has the fresh air vent open and the last (F.W.) also has the driver's window open.

Model	Year	Vol. m^3	Fresh air (L/s)			
				Fan	F.V.	F.W.
Kingswood	1970	5.81	1.05	2.52	2.52	
Volvo	1978	6.48	4.00	20.8	22.0	1363
Commodore	1979	3.81	5.78		85.0	
Pulsar	1984	4.16	0.61	20.2	77.4	
Corolla	1985	5.68	3.00	20.0	149.7	262.2
Falcon	1987	4.44	38.03	164.0	134.5	151.2
Laser	1988	3.48	1.42	4.56	85.1	41.0
Berlina	1989	4.36	2.95	173.0	173.0	
Magna	1989	6.12	6.00	37.0	100.7	987
Astron	1989	5.50	50.0	143.0	136.0	312

Table 3: Loss in tracer concentration in the passenger compartment when driver's door briefly opened fully and closed with fan off and vent closed (Razmovski 1994).

Model name	King.	Comm.	Pulsar	Laser	Berlina
Year of manufacture	1970	1979	1984	1988	1989
Time door open (s)	5.70	3.60	3.27	3.60	3.70
Tracer conc. loss (%)	10.3	33.6	29.8	21.8	19.7

7 Peak Concentrations

Table 4 gives peak mean concentrations for leaks of R290/600a calculated using Equations 2 and 3 and converted to %LEL. The ratio of charge to volume in column 5 is always higher than the last four columns. The multipliers to convert column 5 to a percentage of practical limit (BS4434-1995) are 0.24, 0.44 and 0.97 for refrigerants 12, 134a and 406a respectively used on the same car. For a new design, using R600a the charge to volume ratios can be less than half those in column 5.

Table 4: Expansion valve position, initial charge of R290/600a, ratio of charge to volume and peak average concentration in the passenger compartments of ten Australian cars as a percentage of the lower explosion limit (LEL) for four release scenarios. P=in passenger compartment, E=in engine bay.

Leak type					Sudden	Worst		
Fan is					on			off
Vent is					open		closed	
Model	Year	Valve Pos.	Charge g	Charge %LEL	Peak concentration %LEL			
Kingswood	1970	P	280	120	92	118	118	44
Volvo	1978	P	367	141	46	137	137	13
Commodore	1979	E	420	276	21	0.6		9
Pulsar	1984	E	333	200	18	0.6	3	74
Corolla	1985	P	233	103	7	98	100	17
Falcon	1987	E	433	244	14	0.4	0.3	1.3
Laser	1988	P	233	167	12	157	162	35
Berlina	1989	E	367	210	9	0.3	0.3	17
Magna	1989	P	233	95	9	92	93	8
Astron	1989	P	283	129	9	121	121	1.0

Column 6 of Table 4 gives the concentrations resulting from a sudden major release (Section 2.2). BS 4434–1995 requires for other applications that the practical limit not be exceeded. The practical limit is 20% of the LEL for R290/600a and the seven cars manufactured after 1980 meet it. Values for refrigerants 12, 134a and 406a are not given but they exceed their practical limits for none of these cars.

The last three columns of Table 4 use the worst leak physically possible for the design and operation condition described in Section 4. IAHRA (1996) requires that with fan on and vent open the LEL not be exceeded and column 7 shows six of the vehicles satisfy this. Column 8 shows although closing the fresh air vent where one exists increases the peak concentration, the same cars still satisfy the IAHRA requirement except no fresh air measurement was made for the Commodore.

Column 9 is for leakage when the vehicle is unoccupied with engine and air conditioner off. Any instantaneous complete fracture must result from a pressure increase which may occur immediately after the ignition is turned off. Even if the occupant ignores the cloud, leaving the car drops the concentration (Table 3) making the slower leaks worse. None of the ten cars exceed the LEL.

8 Conclusion

Manufacturers of car air conditioners for R290/600a or R600a should comply with the requirements of BS 4434–1995 for stationary systems. In particular, there should be no screw fittings or elastomer hoses containing refrigerant in the passenger compartment. They should minimize the design initial charge.

An R290/600a retrofitter should for the passenger compartment replace damaged mountings or screw fittings and replace elastomer hoses with metal extensions or add IAHRA (1996) safety valves. Do not retrofit cars without fresh and exhaust air vents. The initial charge should not exceed either 400 g or a third the charge recommended for R12. Do not use mercury-in-glass thermometers.

References

URL: `http://ilm.mech.unsw.edu.au/pub/archive/HC/`

ADC, 1973, *Standards for Australian Aluminium Mill Products*, Metric Edition, The Aluminium Development Council of Australia Ltd, Sydney.

Broek, D., 1982, *Elementary engineering fracture mechanics*, Martinus Nijhoff, The Hague, 469 p.

Boucher, D. F. and Alves, G. E., 1973, *Fluid and Particle Mechanics*, Section 5 of Chemical Engineers' Handbook 5th ed., R.H. Perry and C.H. Chilton editors, pp. 5-43, 5-44.

BS 4434–1995, *Safety and environmental aspects in the design, construction and installation of refrigerating appliances and systems*, British Standards Institution, London, 64 p.

Cai, D., 1996, *Escape of Hydrocarbon Refrigerants in Car Air Conditioning*, M.Eng.Sc. thesis, School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney, 121 p.

Elias, N. N., 1996, *Ignition of High Speed Hydrocarbon Leaks from Car Air-Conditioning Systems*, B.E. thesis, School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney, 144 p.

FORS, 1995, *Australian Design Rule 15/01, Demisting of Windscreen*, Australian Design Rules for Motor Vehicles and Trailers 3rd ed., Federal Office of Road Safety, Department of Transport & Communications, Canberra.

Huber, M., Gallagher, J., McLinden, M., and Morrison, G., 1996, *NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Version 5.0 Users' Guide*, NIST Standard Reference Database 23, U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg MD.

IAHRA, 1996, *Code of Practice for the Use of Hydrocarbon Refrigerants in Motor Vehicle Air Conditioning*, The Independent Australian Hydrocarbon Refrigeration Association, Brisbane, December.

Maclaine-cross, I.L., and Leonardi, E., 1997, *Why hydrocarbons save energy*, AIRAH Journal, vol. 51, no. 6, June, pp. 33–38.

Rajasekariah, C., 1995, *Hydrocarbon Refrigerant Safety in Automobiles*, B.E. thesis, School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney, 140 p.

Razmovski, V., 1994, *Safety of Hydrocarbon Refrigerants for Car Air Conditioning Systems*, B.E. thesis, School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney, 97 p.

Schlichting, H., 1968, *Boundary Layer Theory*, 6th ed., McGraw-Hill, 748 p.

Tosovic, D. R., 1996, *Hydrocarbon Refrigerant Safety in Automobiles*, M.Eng.Sc. thesis, School of Mechanical and Manufacturing Engineering, The University of New South Wales, Sydney, 200 p.